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PAPER CONTAINER
[Kami-yoki]

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Claims

1. A paper container that is made of a laminated body comprising a resin layer made of a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, and paper, characterized in that the density of the paper is 0.60-0.95 g/cm^3, and the rigidity per 1 μm in the length direction is 0.4-0.9 gf·cm.

2. The paper container described in Claim 1, characterized in that the paper contains at least 40 wt% pulp obtained from conifers.

3. The paper container described in Claim 1 or 2, characterized in that a polyethyleneimine system undercoating agent is contained in or coated on the paper.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to a paper container that is suitable for filling with liquid. More specifically, it pertains to a paper container that is made of a laminated body comprising a resin layer made of a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, and paper.

[0002]

Prior art

Paper containers made of a laminated body comprising paper and a resin layer are advantageous because they are light, they can be recovered and reused after they are used, and they have relatively low calorific values, so they have long been used widely as containers for such liquids as fruit juices, alcohol beverages, oils, and detergents. Paper containers made of a laminated body comprising paper and a resin

layer shows differences in terms of blocking property (sometimes referred to also as a barrier property) with respect to gases such as oxygen or water vapor and content flavor retaining property depending on the kind of laminated resin layer, so paper containers utilizing a variety of laminating resin layers have been proposed.

[0003]

Among those resin layers, a layer made of a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid has been known to have excellent characteristics; for example, because it has a gas barrier property, the content is less likely to oxidize or deteriorate; and because it is thermally stable, little harmful decomposed matter is created even when heated for thermal bonding when forming the laminated body into a container. As such, paper containers that are made of a laminated body comprising a resin layer containing an XD-6 structural unit and paper (Japanese Kokai Patent Application No. Sho 53[1978]-119984, Japanese Kokai Patent Application No. Hei 3[1991]-49953, etc.) and a paper container that is made of a laminated body comprising paper further combined with a different kind of polyamide resin layer (Japanese Kokai Patent Application No. Hei 6[1994]-305086), for example, have been proposed. However, when a paper container is produced in accordance with these proposals, fine cracks are likely to be created during a step in which what is called ruling is applied in order to fold the laminated body into the container shape. Also, when in the obtained container is filled with content and stored at room temperature for 1-2 weeks, the container is deformed so badly that the outer appearance deteriorates significantly, resulting in reduced commercial value. This phenomenon is thought to be related to mechanical characteristics and water-absorption property of the resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid.

[0004]

Problem to be solved by the invention

The objective of the present invention is to obtain a paper container that is made of a laminated body comprising a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, whereby a high level of workability can be attained, and a good outer appearance can be maintained with little deformation even when stored with content filled therein.

[0005]

Means to solve the problem

As a result of keen examination of the aforementioned goal, prior to the completion of the present invention, the present inventors found that it can be achieved by a paper container that is made of a laminated body comprising a resin layer made of a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, and paper, characterized in that the density of the paper is 0.60-0.95 g/cm^3, and the rigidity per 1 μm in the length direction is 0.40-0.90 gf·cm.

[0006]

Embodiment of the invention

The paper container of the present invention is made of a laminated body comprising a resin layer made of a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, and paper.

[0007]

In the present invention, a polyamide resin created by means of a polycondensation reaction of metaxylylene diamine and adipic acid refers to a resin that is entirely based on a structural unit created by means of a polycondensation reaction of metaxylylene diamine and adipic acid, a resin that is based on a structural unit created by means of a polycondensation reaction of metaxylylene diamine as the main component and small amounts of paraxylylilene diamine and adipic acid (The structure created by means of a polycondensation reaction of metaxylylene diamine and adipic acid and the structure created by means of a polycondensation reaction of metaxylylene diamine as the main component and small amounts of paraxylylene diamine and adipic acid may be referred to as an XD-6 structural unit, hereinafter), or a polyamide resin created by means of copolymerization of m- or/and p-xylylene diamine and adipic acid as the main components and a different kind of diamine or dicarbonic acid. Ethylene diamine, tetramethylene diamine, pantamethylene [sic; pentamethylene] octamethylene diamine, hexamethylene diamine, octamethylene diamine and octamethylene diamine [sic], for example may be mentioned as examples of diamines that can be used for the copolymerization. In addition, sebacic acid, suberic acid, glutaric acid, and azelaic acid, for example, may be mentioned as examples of carbonic acids that can be used for the copolymerization. In the case of a copolymerized polyamide resin, it is desirable that the XD-6 structural unit content is at least 60 mol% in order to appropriately maintain the gas barrier property and the crystallinity of the resin.

[0008]

In addition, a layer created by mixing a polyamide resin that contains at least 90 mol% of XD-6 structural units with another polyamide resin may be used as the polyamide layer containing the XD-6 structural unit. Nylon 6, nylon 66, nylon 46, nylon 610, and nylon 12, for example, may be mentioned as examples of the other amide resin to be mixed. Furthermore, small amounts of resins other than

polyamide, for example, polyethylene, ethylene-vinyl alcohol copolymer, ethylene-acrylic acid copolymer, ethylene-maleic anhydride copolymer, polyester and polycarbonate, may be mixed when so desired. In the case of a resin blend, it is desirable that it contains at least 60 wt% of polyamide resin that contains at least 90 mol% of XD-6 structural units in order to avoid excessive deterioration of the gas barrier property.

[0009]

Although the resin layer of the present invention may be monolayer or multilayer, comprising at least 2 layers, at least one of the layers must be formed from a polyamide resin containing the XD-6 structural unit. A complex resin layer comprising a polyamide resin containing the XD-6 structural unit and another resin layer may be utilized also. Such polyesters and polycarbonates as polyethylene, polypropylene, polyvinyl alcohol, ethylene-vinyl alcohol copolymer, polyvinylidene chloride, polystyrene, polyethylene terephthalate may be mentioned as examples of resins to be complexed with the polyamide resin containing the XD-6 structural unit, and these resin layers may be unstretched, or they may be stretched uniaxially or biaxially. Although the thickness of the resin layer is dependent on the kind and the properties of the contents of the paper container, 5-40 μm is desirable.

[0010]

In addition, a metal layer, such as an aluminum foil or a tin foil, may be complexed with those resin layers in order to add a light-blocking property or to further improve the gas barrier property. Although the polyamide resin containing the XD-6 structural unit can be provided at an arbitrary position on the laminated body that constitutes the paper container of the present invention, preferably, it is provided on the inner side of the paper when forming the container. Furthermore, it is preferably provided between the paper and a heat-sealing resin layer, such as low-density polyethylene, linear polyethylene,

low-density linear polyethylene, or polypropylene, that is suitable for the thermal bonding during the formation of the container.

[0011]

No special restriction is imposed in terms of the paper used for the laminated body in the present invention as long as it is made using natural fibers, synthetic fibers, or their mixture. Such wood fibers as softwood pulp and hardwood pulp; pulp of such vegetable fibers as cotton yarn, sugarcane, and bamboo; and such animal fibers as wool and silk may be mentioned as natural fibers to be used for the paper-making. In addition, polyethylene, polypropylene, polyester, polyamide, and acetylcellulose, for example, may be mentioned as synthetic fibers. Among the papers obtained from these fibers, paper obtained from wood pulp is preferable in terms of the mechanical and thermal properties of the paper; and a paper made from wood pulp that contains at least 40 wt% of softwood pulp when dried is particularly desirable in terms of improved tensile strength.

[0012]

In addition, it is desirable that an olefin system, polyethyleneimine system, isocyanate, polyester system, polyurethane system, or vinyl system undercoating agent is contained in the paper used in the present invention during the paper-making, or it is coated on the paper after the paper-making in order to improve the bonding property with the resin layer. Among these undercoating agents, a polyethyleneimine system undercoating agent is preferable. The density of the paper used in the present invention must be 0.60-0.95 g/cm^3, or preferably 0.65-0.90 g/cm^3. If the paper density is lower than 0.60 g/cm^3, a fine crack is likely to be created in the paper during the ruling step for folding the laminated body into the container shape, and the production yield of good paper containers drops significantly. This is thought to result from the fact that because the elasticity coefficient of the

polyamide resin layer containing the XD-6 structural unit is relatively high, the height of the ruling line must be set higher than when a different resin is layered. When the paper density exceeds 0.95 g/cm^3, not only is the paper hard to bend, but the elasticity coefficient of the polyamide resin layer containing the XD-6 structural unit is also high, so that bending along the ruling line becomes harder to achieve, and the obtained container has a bad shape. Furthermore, in the present invention, the paper density is defined using a value measured in accordance with "Densities of paper and pressboard and testing method" of JIS P1118.

[0013]

Furthermore, the rigidity in the length direction of the paper used in the present invention must be 0.40-0.90 gf·cm per 1 μm thickness, or preferably, 0.45-0.80 gf·cm. Here, length direction of paper refers to the length direction during the paper-making. When making containers using paper, the length direction of the paper is usually placed parallel to the level at which the gravity of the content is applied. If the rigidity of the paper in the length direction is less than 0.40 gf·cm per 1 μm thickness, when the obtained carton-like container is filled with a content with high water content, such as a fruit juice or an alcoholic beverage, and stored for 1-2 weeks, the bottom part of the container swells up as the quadrangular bent parts that constitute the horizontal cross section of the body part of the container are deformed into a circular shape, and the outer appearance deteriorates significantly. In addition, if the rigidity of the paper in the length direction exceeds 0.90 gf·cm per 1 μm thickness, the height of the ruling line must be set significantly high during the ruling step for bending the laminated body into the container shape. As a result, the resin layer is destroyed (pin hole) at a small part, and the gas barrier property drops, so that the content becomes more likely to deteriorate. Furthermore, in the present invention, rigidity of paper is defined using a value that is measured in accordance with "Pressboard

rigidity testing method using gravimetric bending method" of JIS P8125 and converted into a value per 1 μm.

[0014]

Methods that may be used for obtaining the laminated body comprising the resin layer and the paper include a method in which respective resin layers used to preform a film-like resin layer, and the resin layer and paper, are dry-laminated together using a urethane system, acrylic system, or polyester system adhesive; a method in which resin layers preformed into a film-shape are sandwich-laminated to form a resin layer; a method in which resins to be used to form a resin layer are extruded and laminated together sequentially; a method in which multiple extruders with feed blocks are used for simultaneous melt-extrusion of many layers to be laminated; or a method in which the sandwich-lamination, the dry-lamination, and the melt-extrusion-lamination are combined arbitrarily.

[0015]

Furthermore, a highly adhesive resin layer may be provided, and a physical science [sic; possibly physicochemical] treatment such as a corona treatment, a plasma treatment, or an ozone treatment may be performed during or before the lamination step in order to improve the bonding between the respective resin layers and between the resin layer and the paper. Polyethylene, ethylene-vinyl acetate copolymer, maleic anhydride denatured ethylene-vinyl acetate copolymer, maleic anhydride denatured polyethylene, ethylene-methacrylate copolymer, ethylene-methyl methacrylate copolymer, maleic anhydride denatured polypropylene, and an ionomer may be mentioned as such highly adhesive resins.

[0016]

A desired paper container can be obtained through ordinary container production steps, that is, a step in which a target container in its unfolded state is punched from a laminated body comprising a resin layer, that contains at least 1 polyamide resin layer containing the XD-6 structural unit obtained in said manner, and paper, a step in which ruling lines are added, a step in which the bonded parts of the body part are bent outwardly (skiving) as needed to prevent the content from coming into contact with the cross-sections of the paper, a step in which the body part is bonded, and a step in which the bottom and top parts are formed.

[0017]

The paper container of the present invention obtained in the aforementioned manner can be formed into cartons or cups of various shapes and sizes, and they are suitable as containers for fruit juices, such dairy beverages as milk and yogurt drinks, alcoholic beverages, mineral waters, such dietary oils as salad oils, industrial oils, and detergents.

[0018]

Application examples

The present invention will be explained more specifically below using application examples. However, the present invention is not restricted to those application examples. Furthermore, methods for measuring respective properties described in the application examples and comparative examples are as follows.

[0019]

(1) Amount of deformation of the container

Quadrangular tubular parts of a paper container having an upright quadrangular tubular body part that was sealed off at the top and the bottom were placed partially in contact with a plane formed in the horizontal direction and a plane formed in exactly the perpendicular direction while positioning the container in such a manner that one side at the top of the quadrangular tubular parts was parallel to the vertical plane; and the distance between the aforementioned parallel line and the vertical plane was measured under said condition. If poor bending property is provided at the quadrangular tubular parts during the container production process, or when the container gets deformed due to swelling (body swelling) at the bottom of the quadrangular tubular parts during the storage of the container while filled with content, this measurement value increases. Here, a container that showed at least 10 mm as this value was considered a good container.

(2) Surface defect

A testing medium (red check medium), that emits light in the event of a surface defect associated with a fine crack on paper, was applied to the 4 bent parts at the quadrangular tubular parts of each of 100 containers in order to check the quantity of defects, and the quantity observed per 100 containers was shown. Containers that showed 10 or more defects were considered defective containers.

(3) Gas barrier property of container

A good gas barrier property was determined when the respective surfaces at the top of the quadrangular tubular parts of a container were vertical, or when they were bent toward the inner side of the container, after it was filled with 65°C hot water and stored at room temperature for 3 weeks, and a poor gas barrier property was determined when the respective surfaces at the top of the quadrangular

tubular parts were bent toward the outside of the container. The pressure inside the container is reduced when the container returns to room temperature after filled with hot water; and the respective surfaces at the top of the quadrangular tubular parts either remain vertical or get bent toward the inner side of the container when the gas barrier property is good, but the respective surfaces get bent toward the outer side of the container when the gas barrier property is poor.

(4) Relative viscosity of resin

A value obtained by measuring the viscosity of a solution that was prepared by dissolving 1 g of resin in 100 mL of 96% sulfuric acid at 25°C was used to this end. It was calculated using the following formula.

Relative viscosity = number of seconds it takes for resin-sulfuric acid solution to drop/number of seconds it takes for sulfuric acid to drop

[0020]

<u>Application Example 1</u>

While using a coextrusion laminator equipped with multiple extruders, feed blocks, and T dies to apply a corona treatment to the surface of paper that contained 90 wt% softwood pulp and 10 wt% hardwood pulp with a basis weight of 405 g/m^2, density of 0.75, and rigidity of 0.72 gf·cm per 1 μm thickness in the length direction, a resin created by laminating 10 μm of polyamide resin having a relative viscosity of 3.6 that was synthesized using m-xylylene diamine containing a small amount of p-xylylene diamine and adipic acid, 10 μm of denatured polyolefin "Modic F2300K" (manufactured by Mitsubishi Chemical Corp.), and 60 μm of low-density polyethylene "Novatec L300" (manufactured by Mitsubishi Chemical Corp.) were laminated in said order in the T dies such that a polyamide resin layer comprising only the XD-6 structural unit came into contact with the paper. Furthermore, 20 μm of the

low-density polyethylene "Novatec L300" (manufactured by Mitsubishi Chemical Corp.) was extruded and laminated to the opposite side of the aforementioned laminated paper in order to obtain a laminated body. After the laminated body was formed into a sleeve shape through the respective steps for punching the aforementioned laminated body, ruling, skiving, and thermal bonding of the body part by flame heating, a paper container, wherein each side of the quadrangular tube is 85 [sic; 8.5] cm, the height is 25.7 cm, and the top part is formed into a roof shape (gable top), that was filled with 1.8 L of 65°C hot water was obtained using a thermoforming filling device for an alcohol beverage. After the water-filled paper container was stored for 3 weeks while it was kept upright, the quantity of surface defects was checked, the amount of deformation of the paper container was measured, and its gas barrier property was evaluated. The results are shown in Table 1.

[0021]

Comparative Example 1

A paper container, wherein each side of the quadrangular tube was 85 cm, the height was 25.7 cm, and the top part was formed into a roof shape (gable top), that was filled with 1.8 L of water was obtained in the same manner as that in Application Example 1, except that paper having a basis weight of 420 g/m^2, density of 0.55, and rigidity of 0.57 gf·cm per 1 μm thickness in the length direction was used. The evaluation results are shown in Table 1.

[0022]

Application Example 2

A paper container, wherein each side of the quadrangular tube was 7 cm, the height was 19.5 cm, and the top part was formed into a roof shape (gable top), that was filled with 1.0 L of water was obtained in the same manner as that in Application Example 1, except that paper was used that contained 70 wt%

softwood pulp and 30 wt% hardwood pulp with a basis weight of 310 g/m^2, density of 0.82, and rigidity of 0.65 gf·cm per 1 μm thickness in the length direction, and a polyamide resin blend comprising 70 wt% of the polyamide resin used in Application Example 1 and 30 wt% nylon 66 resin with a relative viscosity of 3.3 was used as the polyamide resin. The evaluation results are shown in Table 1.

[0023]

Comparative Example 2

A paper container, wherein each side of the quadrangular tube was [sic; no measurements given], and the top part was formed into a roof shape (gable top), that was filled with 1.0 L of water was obtained in the same manner as that in Application Example 2, except that paper was used that was made only of softwood pulp, with a basis weight of 315 g/m^2, density of 0.78, and rigidity of 0.35 gf·cm per 1 μm thickness in the length direction, and precoated with polyethyleneimine system undercoating agent "DicDry AC108" (manufactured by Dainippon Ink and Chemicals, Inc.) by means of gravure printing. The evaluation results are shown in Table 1.

[0024]

Application Example 3

While using a laminator equipped with multiple extruders and metal mouth pieces capable of extrusion-lamination and sandwich-lamination to apply a corona treatment to the surface of paper that contained 80 wt% softwood pulp and 20 wt% hardwood pulp with a basis weight of 430 g/m^2, density of 0.79, and rigidity of 0.63 gf·cm per 1 μm thickness in the length direction, and the surface of a film on which 15 μm of low-density polyethylene was laminated, wherein the film was made of a mixture comprising 70 wt% of resin made only of the DX-6 structural unit and 30 wt% nylon 66 resin, while prelaminated with 15 μm of low-density polyethylene on one surface and 60 μm on the other surface,

were sandwich-laminated using 15 μm-thick low-density polyethylene "Petrocene 204" (manufactured by Tosoh Corp.). Then, 20 μm of the low-density polyethylene "Petrocene 204" (manufactured by Tosoh Corp.) were extruded and laminated to the opposite surface of the paper in order to obtain a laminated body comprising the resin layers and the paper. A quadrangular tubular paper container with a roof-shaped top (gable top) filled with 1.8 L of water was obtained using this laminated body in the same manner as that in Application Example 1. The evaluation results are shown in Table 1.

[0025]

TABLE 1

		1 坪量 g/m^2	2 密度 g/cm^3	3 こわさ gf·cm	4 表面欠陥 コ/缶100本	5 容器変形量 mm	6 気体の遮断性
7	実施例 1	405	0.75	0.72	0	4	良 9
8	比較例 1	420	0.55	0.57	26	16	不良 10
7	実施例 2	310	0.82	0.65	0	6	良 9
8	比較例 2	315	0.78	0.35	10	15	不良 10
7	実施例 3	430	0.79	0.63	1	5	良 9

Key: 1 Basis weight

2 Density

3 Rigidity

4 Surface defect

Quantity/100 containers

5 Amount of deformation of container

6 Gas barrier property

7 Application Example __

8 Comparative Example __

9 Good

10 Bad

[0026]

As it is clear from the results shown in Table 1, while the paper container of the present invention exhibits excellent performance in that it is subject to little surface defect and deformation, when the density (Comparative Example 1) and the rigidity in the length direction (Comparative Example 2) fall out of the range of the present invention, surface defects and deformation take place, and a good paper container can no longer be obtained.

[0027]

Effects of the invention

With the paper container of the present invention, even when a liquid beverage or an oil is filled and stored for a long period of time, deterioration and alteration of content never take place. What is more, because its outer appearance remains good, the problem that it becomes difficult to take out of a display shelf due to deformation will never happen.